The Distribution and Ecological Risk Assessment of Heavy Metals in Mudflat Sediments at Mai Po Ramsar Site

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Introduction

- Mudflat is an intertidal zone located between sea and land in coastal wetlands which provide important ecological functions such as habitats for sheltering wildlife and carbon sequestration for helping climate change, especially in Mai Po Ramsar site which served as a key winter home for migratory birds (Man et al., 2021).
- Changes of mudflat ecosystems are closed related to human activities such as urbanization and industrialization. River water carried heavy metals released from human activities flows into coastal areas and leads to accumulation of heavy metals in mudflat sediments (Li et al., 2023).
- Heavy metals are widely distributed in sediment environments because they are naturally occurring and are non-degradable elements. Accumulation of heavy metals in sediment raises ecological risk to benthic biota and gigantic organisms and threats human health through the food chains (Zaynab et al., 2022).
- Mai Po Nature Reserve, a RAMSAR in south China located in Inner Deep Bay of Pearl River Delta area was considered possibly the biggest pollution hot spot in East Asia (Li et al., 2016).
- Identification of ecological risks of heavy metals in Mai Po mudflat sediment can help to conserve the Ramsar site and protect migratory birds from heavy metal pollution.
- This study aims to 1) determine distribution and identify the source of heavy metals in mudflat sediment of Mai Po using enrichment factor (EF), geo-accumulation index (Igeo), and Pearson correlation analysis, and 2) to assess their ecological risk to benthic and gigantic organisms using sediment quality guidelines.

Methodology

Sample collection and heavy metal analysis

Sediment samples (top 10 cm) were collected from four sampling sites in mudflat of Mai Po. Triplicate samples were collected from each sampling site, with one replicate sample contained around 1 kg of fresh sediment collecting from a quadrat (1 m x 1 m), and each replicate sample was around three meters away from the other (Figure 1). Samples were transported to the laboratory immediately after sample collection. The method of sample preparation and heavy metals analysis was summarised in Figure 2.

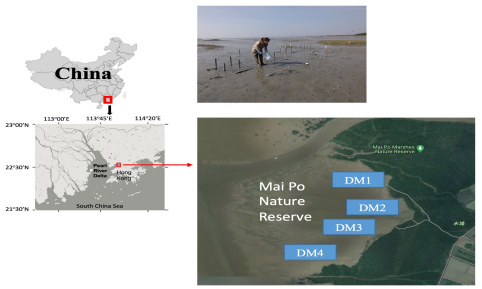

Fig. 1. Sampling site of Mai Po Nature Reserve

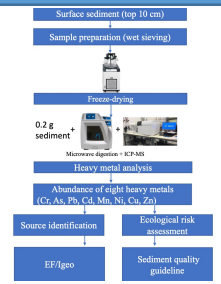

Fig. 2. Heavy metals analysis used in this study from sample preparation to data analysis

Results:

Heavy metals in mudflat sediment of Mai Po

8 heavy metals were detected in all sediments, with concentrations of Mn, Zn, Cr, Cu, Pb, Ni, As and Cd ranging from 421 to 543, 275 to 299, 73.1 to 94.3, 71.2 to 73.9, 62.9 to 65.6, 30.1 to 32.8, 15.4 to 16.6 and 0.77 to 0.95 μg g^{-1}, respectively, followed a decreasing order of Mn > Zn > Cr > Pb > Cu > Ni > As > Cd (Table 1).

Sediment quality guideline

All metals (except Cd) in sediments collected from mudflat of Mai Po exceeded sediment quality standard set by the United States Environmental Protection Agency. The average concentrations of Cr, Pb, Ni, Cu, As, and Cd were above TEL but below PEL, indicating that these metals might occasionally pose negative biological effects on benthic organisms. It should be noticed that the average concentration of Zn in mudflat sediment was above PEL, showing that Zn frequently exerts an adverse biological effect on benthic organisms (Table 1).

Enrichment factor (EF) and geo-accumulation index (Igeo)

The EF values of Cr, Ni and As were below 1.5 and Igeo values of these three metals were < 0 but the EF value of Zn and Cu were higher than 2 and Igeo values of these two metals were higher than 1 in all sediment. These results indicated that the mudflat sediment of Mai Po was not polluted by Cr, Ni, and As, their occurrence was because of natural process. However, the mudflat sediment was moderately polluted by Zn and Cu, their accumulation was due to human activity (Figure 3).

Pearson correlation of heavy metals in mudflat sediment

Zn is significantly correlated with Ni and Cu ($p <$ that agric0.01) and Pb is significantly correlated with Ni ($p < 0.001$). These results suggested that agricultural and industrial processes such as mining and use of fertilizer might be the source of pollution affecting the mudflat ecosystem (Zhang et al., 2018).

Sites	Mn	Zn	Cr	Cu	Pb	Ni	As	Cd
DM1	421± 39.2b	275± 29.5	94.3± 34.1	71.2± 2.9	63.3± 1.0	30.1 ± 2.4	15.4 ± 0.3b	0.77 ± 0.3
DM2	447± 14.9b	287± 5.4	80.2± 7.0	73.3± 1.5	62.9± 2.3	31.4 ± 0.4	16.6 ± 0.5a	0.95 ± 0.1
DM3	487± 21.5ab	299± 14.2	73.1± 3.8	73.9± 1.3	65.6 ± 0.7	32.8 ± 0.2	15.9 ± 0.4ab	0.82 ± 0.1
DM4	543± 25.8a	290± 4.3	78.1± 5.6	71.7± 1.7	65.0 ± 0.8	32.1 ± 0.4	16.2 ± 0.4ab	0.94 ± 0.2
Average	474±53.2	288±2.04	82.4±17.2	72.6±2.0	64.2±1.6	31.6±1.4	16.1±0.5	0.87±0.1
USEPA	121	150.0	42.3	31.6	35.8	27.3	9.8	0.9
TEL	-	123.0	37.3	35.7	35.0	18.0	5.9	0.6
PEL	-	271.0	90.0	197.0	91.3	36.0	17.0	3.5

USEPA = United States Environmental Protection Agency soil quality standard; TEL: threshold effect level; PEL: probable effect level; -: data not available

Table 1 : Heavy metal concentrations (μg g^{-1}) in sediments of mudflat in Mai Po wetland (mean ± SD of three replicates are shown). Differences in the concentrations of these heavy metals between the sampling sites were indicated by lowercase letters according to ANOVA followed by Tukey post-hoc t-test at $p \leq 0.05$.

Metals	Cr	Mn	Ni	Cu	Zn	As	Cd	Pb
Cr	1.00							
Mn	-0.30	1.00						
Ni	0.03	0.50	1.00					
Cu	0.38	-0.21	0.55	1.00				
Zn	0.00	0.05	0.77**	0.73**	1.00			
As	0.37	0.24	0.22	0.55	0.15	1.00		
Cd	0.18	-0.39	-0.20	0.17	-0.09	0.06	1.00	
Pb	-0.02	0.56	0.83***	0.39	0.51	0.13	-0.14	1.00

Table 2 : Pearson correlation coefficient matrix for heavy metals of sediment samples collected mudflat in Mai Po. ** indicates that correlation is significant at 0.01 level and *** indicates that correlation is significant at 0.001 level (two-tailed)

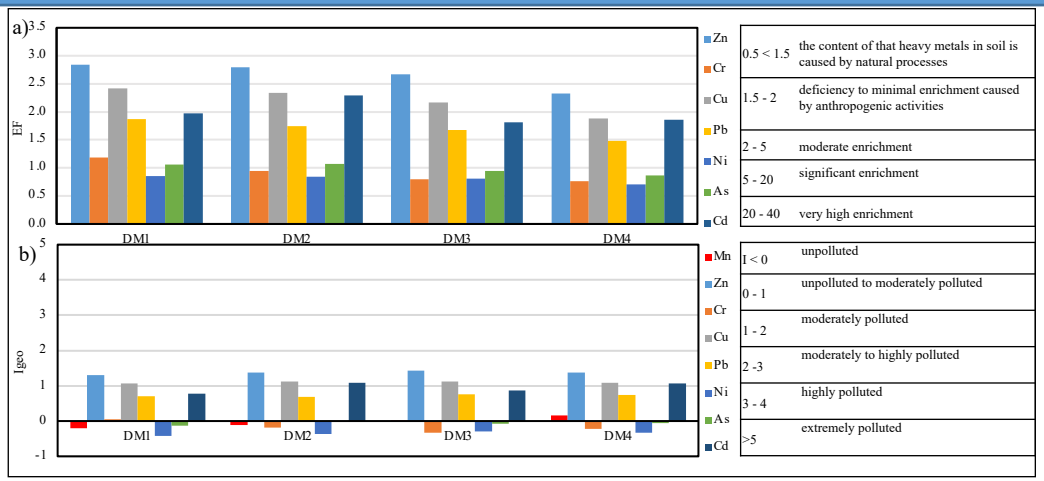

Fig.3. a) Enrichment factor (EF) and b) geo-accumulation index (Igeo) of heavy metals in mudflat sediment of Mai Po (average concentrations of heavy metals were used to calculate the values of EF and Igeo. Manganese (Mn) was used as the reference element in the calculations of EF).

Conclusion:

- Mudflat sediment of Mai Po Ramsar has been polluted by Zn, Cu, Pb, and Cd.
- Pollution of Zn in the sediment should be drawn more attention as its adverse negative effects on benthic organisms have been observed in the mudflat sediment of Mai Po.
- Actions in prevention of heavy metal pollution from agricultural and industrial processes should be applied in order to conserve the mudflat ecosystem and protect migratory birds.

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